Red to Near-Infrared Luminescent Materials Activated by Transition Metals for in vivo Imaging and Telecommunication Application(Digest_要約)

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We start from two applications of luminescent materials showing red or near-infrared emission: *in vivo* imaging and telecommunication in Chapter 1. Brief histories, important progresses, some existing problems, and perspectives on these two fields are introduced. As described in the first part, an *in vivo* imaging system by using red or NIR persistent nano-particles was proposed by Chermont et al. This approach was followed by other research groups. Exploration of novel red or NIR persistent phosphor as well as investigation on their mechanism was also triggered. In the second part, the original model, Tyndall experiment, for modern telecommunication is described. There are two important landmarks in the development of telecommunication system: the paper by C. Kao from Standard Telecommunication Laboratories (UK) discussing the feasibility of using low-loss glass fiber for telecommunication as well as the development and wide usage of Erbium-doped fiber amplifiers.

In Chapter 2, basic knowledge on luminescence is summarized. Starting from general introduction on phenomenon of absorption and emission (luminescence), luminescence from normal localized center (emission from delocalized center or defects or thermal irradiation are not included) is classified into four groups: d-d transitions from transition metals, f-f transitions and f-d transitions from rare earth ions, and s-p transitions from main group elements. Emphasis is put on d-d transitions since this is the major type of luminescence center in this thesis. Selection rules governing the electron transition, including absorption and luminescence is discussed. As two important luminescence centers for red or NIR luminescence, Cr^{3+} in octahedral field and Cr^{4+} in tetrahedral field are specially introduced in Chapter 2. In the final part, some processes playing important roles in the dynamics of luminescence (including persistent luminescence) are introduced: energy transfer, trapping, and detrapping process.

In chapter 3, we made a systematic investigation on the optical properties of non-doped and Cr-doped $Zn_xGa_2O_{3+x}$ spinel crystals. Absorption, photoluminescence excitation, and persistent luminescence excitation spectra indicated that the bottom of conduction band (CB) was affected (i) by compositional deviation from stoichiometry or (ii) by atmosphere control in a similar way. By constructing energy level diagram, a broad distribution of trap depth in a Cr^{3+}-doped $Zn_xGa_2O_4$ sample with composition of Zn excess or in one prepared in O_2 was attributed to lowering of CB bottom, which resulted in faster decay of persistent luminescence in these two samples. Defect chemical reactions revealed that the anti-sites species of Zn'_{Ga} may be the reason of the lowering of conduction band bottom. A self-redox effect of Cr ions induced by compositional deviation was well explained by the defect reactions. The investigation indicated that the composition with slightly Zn deficiency is important to obtain a narrow distribution of trap depth and longer persistent luminescence, however the self-reduction effect of Cr ions in the composition of Zn deficiency should be considered.

In chapter 4, Bi_2O_3 was proved to be an effective codopant to enhance red persistent luminescence in Cr^{3+}-doped $Zn_{0.98}Ga_2O_{3.98}$ spinel. The Cr-Bi-codoped $Zn_{0.98}Ga_2O_{3.98}$ phosphors showed about 10 times higher persistent luminescence intensity than the Cr-singly-doped phosphors. The radiance (in $mW \cdot Sr \cdot m^{-2}$) of persistent luminescence in $Zn_{0.98}Ga_2O_{3.98}$:Cr,Bi phosphors was comparable to that in commercialized $SrAl_2O_4$:Eu,Dy phosphors. Increases of Cr^{3+} absorption and photoluminescence were also observed in the Cr-Br-codoped $Zn_{0.98}Ga_2O_{3.98}$ sample. The obtained results suggest that Bi_2O_3 may play a critical role in stabilizing Cr^{3+} in $Zn_{0.98}Ga_2O_{3.98}$ spinel. Also, we compared TL curves of $Zn_{0.98}Ga_2O_{3.98}$:Cr and $Zn_{0.98}Ga_2O_{3.98}$:Cr,Bi, which were almost unchanged by Bi_2O_3 co-doping. This result indicated that the key defects responsible for Cr^{3+} persistent luminescence in $Zn_{0.98}Ga_2O_{3.98}$ crystals. Also, the key defects are considered as intrinsic defects (not introduced by any dopants), since the defects are shown to be almost identical in Cr^{3+}-activated and Mn^{2+}-activated persistent phosphors.

In Bi_2O_3 singly doped $ZnGa_2O_4$ crystals, White long-lasting persistent luminescence covering the whole visible region in Bi^{3+}-doped $ZnGa_2O_4$ ceramics is reported. The afterglow luminescence can be observed for several tens of minutes after 360 nm or 280 nm excitation. Photochromism is also observed during ultra-violet excitation. The persistent luminescence and photochromism are considered to originate from electron trapping by defect centers in the $ZnGa_2O_4$ crystals. The Bi^{3+}-doped $ZnGa_2O_4$ ceramics are expected to be potential white-color afterglow phosphors.

As discussed in Chapter 5, thermoluminescence peaks for Cr^{3+} emissions shift to higher temperature due to the partial substitution of Al for Ga sites in $Zn_{0.98}Ga_2O_{3.98}$:Cr,Bi phosphors, which indicates that the electron traps responsible for the red persistent luminescence are tuned to deeper levels by Al-doping. Al-containing phosphors with deeper traps showed a lower persistent luminescence intensity than Al-free samples at 20 °C because the ambient thermal energy is too low to release trapped electrons in deeper levels; however, the Al-containing persistent phosphors perform better at 80 °C with greater thermal energy. At 20 °C, the trapped electrons in the Al-containing phosphors can be efficiently released with the assistance of additional NIR photostimulation. Especially, experiment by using pulsed NIR photostimulation was demonstrated. The pulsed NIR photostimulation presented in this experiment worked as a trigger for the enhanced persistent luminescence. Without the trigger, the deep-trapped electrons were released at a relatively slow rate (natural decay), which can be stored for a long time. Only with the trigger can intense emission be detected, which can highly improve the signal to noise ratio (S/N) in detecting systems. NIR photostimulated red persistent luminescence (NIR-to-red mode) as presented in the Al-containing $Zn_{0.98}Ga_2O_{3.98}$:Cr,Bi phosphors could be a promising technique for new *in vivo* imaging systems.

In Chapter 6, transparent glass ceramics containing Li_2ZnSiO_4:Fe nano-crystals were prepared by melt-quenching method followed by post heat-treatment process. The as-prepared glasses and glass ceramics showed red to near-infrared photoluminescence centered at 730 nm, ascribed to Fe^{3+} ions in tetrahedral coordination. The intensity of the photoluminescence was enhanced by two technologically

simple techniques - the valence state of irons was controlled from Fe^{2+} to Fe^{3+} ions by using oxidizing agents, while the coordination state was compulsorily converted from octahedral to tetrahedral symmetry by performing a ceramization process. The presence of Fe^{2+} ions was considered as a major origin for Fe^{3+} photoluminescence quenching. Oxidation of Fe^{2+} and conversion of Fe^{2+} ions into tetrahedral symmetry contribute to suppression of energy transfer from Fe^{3+} emitters to Fe^{2+} quenching centers.

In Chapter 7, we report on near-infrared photoluminescence studies in $Ca_{1-x}CuSi_4O_{10}$: Yb_x (x = 0.00-0.10) polycrystals by means of diffuse reflection, photoluminescence, excitation spectra and luminescence decay analysis. The samples show intense absorption bands at 540, 630, 800 nm due to Cu^{2+}: $^2B_{1g}\rightarrow{}^2B_{2g}$, ^2E_g, $^2A_{1g}$ transitions. Under the excitation, the samples show efficient photoluminescence at 920 nm from Cu^{2+} and 1007 nm from Yb^{3+}, respectively. With increasing of Yb concentration, the PL intensity of Yb^{3+} increases obviously, while that of the Cu^{2+} decreases slightly. A probable energy transfer mechanism can be proposed on the basis of decay curves and temperature-dependent photoluminescence spectra.

In Chapter 8, transparent glass ceramics containing Li_2MgSiO_4, $LiZnSiO_4$, Mg_2SiO_4, and Zn_2SiO_4 were successfully prepared. The Li_2ZnSiO_4 glass ceramics showed high quantum yield of Cr^{4+} NIR emission. This sample is promising for further investigation, e.g. potential amplification and laser output. Temperature dependence of Cr^{4+} NIR emission in the Li_2MgSiO_4 glass ceramic was also investigated. Finally, absorption and NIR emission spectra in these four transparent glass ceramics were compared. The interesting tunability of NIR emission and shift of absorption was explained by using Tanabe-Sugano diagram to calculate crystal field intensity.